

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 814 522 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

29.12.1997 Bulletin 1997/52

(51) Int. Cl.⁶: **H01M 4/48**, H01M 10/40,
H01M 4/58

(21) Application number: 97110038.3

(22) Date of filing: 21.10.1994

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 22.10.1993 JP 264995/93
27.01.1994 JP 7760/94
24.02.1994 JP 26745/94
28.02.1994 JP 30206/94
11.03.1994 JP 66422/94

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
94116643.1 / 0 651 450

(71) Applicant:
FUJI PHOTO FILM CO., LTD.
Kanagawa (JP)

(72) Inventors:
• **Idota, Yoshio**
Minami-Ashigara-shi, Kanagawa-ken (JP)

• **Mishima, Masayuki**
Minami-Ashigara-shi, Kanagawa-ken (JP)
• **Miyaki, Yukio**
Minami-Ashigara-shi, Kanagawa-ken (JP)
• **Kubota, Tadahiko**
Minami-Ashigara-shi, Kanagawa-ken (JP)
• **Miyasaka, Tsutomu**
Minami-Ashigara-shi, Kanagawa-ken (JP)

(74) Representative:
Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann Eitle,
Patent- und Rechtsanwälte,
Arabellastrasse 4
81925 München (DE)

Remarks:

This application was filed on 19 - 06 - 1997 as a
divisional application to the application mentioned
under INID code 62.

(54) Nonaqueous secondary battery

(57) A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt is disclosed, in which the negative electrode active material contains (1) a compound capable of intercalating and deintercalating lithium comprising an atom of the group IIIB, IVB (except for Si) or VB of the periodic table, (2) an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB (except for Si), and VB of the periodic table, or (4) a compound of the metal of the group IIIB, IVB (except for Si) or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium. The nonaqueous secondary battery of the invention exhibits improved charge and discharge characteristics and improved safety.

Description

FIELD OF THE INVENTION

5 This invention relates to a nonaqueous secondary battery having improved charge and discharge cycle characteristics and improved safety.

BACKGROUND OF THE INVENTION

10 Negative electrode active materials for nonaqueous secondary batteries typically include metallic lithium and lithium alloys. The problem associated with these active materials is that metallic lithium grows dendritically during charging and discharging to cause an internal short circuit, involving a danger of ignition because of high activity of the dendritically metal per se. To solve the problem, a calcined carbonaceous material capable of intercalating and deintercalating lithium has recently been put to practical use. However, since the carbonaceous material has electrical conductivity by itself, metallic lithium is sometimes precipitated on the carbonaceous material at the time of an overcharge or a rapid charge. It eventually follows that lithium grows dendritically thereon. This problem has been dealt with by altering a charger or reducing the amount of the positive electrode active material to prevent an overcharge. Where the latter solution is adopted, however, the limited amount of the active material leads to a limited discharge capacity. Further, the carbonaceous material has a relatively low density and therefore a low capacity per unit volume. Thus, the discharge capacity is limited by both the amount of the active material and the capacity per unit volume.

In addition to metallic lithium, lithium alloys and the above-mentioned carbonaceous material, negative electrode active materials so far proposed include TiS_2 and LiTiS_2 which are capable of intercalating and deintercalating lithium (U.S. Patent 3,983,476); transition metal oxides having a rutile structure, such as WO_2 (U.S. Patent 4,198,476), spinel compounds, such as $\text{Li}_x\text{Fe}(\text{Fe}_2)\text{O}_4$ (JP-A-58-220362, the term "JP-A" as used herein means an "unexamined published Japanese patent application"); a electrochemically synthesized lithium compound of Fe_2O_3 (U.S. Patent 4,464,447); a lithium compound of Fe_2O_3 (JP-A-3-112070); Nb_2O_5 (JP-B-62-59412 (the term "JP-B" as used herein means an "examined published Japanese patent application") and JP-A-2-82447); FeO , Fe_2O_3 , Fe_3O_4 , CoO , Co_2O_3 , and Co_3O_4 (JP-A-3-291862); amorphous V_2O_5 (JP-A-4-223061); and transition metal oxides having their basic crystal structure changed by intercalation of a lithium ion (EP 567149). Any of these known compounds has a high oxidation-reduction potential, failing to provide a nonaqueous secondary battery having a discharge potential as high as 3 V and a high capacity.

SnO_2 or Sn compounds are used as an active material of lithium batteries as in $\text{Li}_{1.03}\text{Co}_{0.95}\text{Sn}_{0.04}\text{O}_2$ as a secondary battery positive electrode active material (EP 86-106301); SnO_2 -added V_2O_5 as a secondary battery positive electrode active material (JP-A-2-158056); SnO_2 -added $\alpha\text{-Fe}_2\text{O}_3$ (preferred SnO_2 content: 0.5 to 10 mol%) as a secondary battery negative electrode active material (JP-A-62-219465); and SnO_2 as a primary battery positive electrode active material (Denki Kagaku oyobi Kogyo Butsuri Kagaku, Vol. 46, No. 7, p. 407 (1978)). With reference to the use of SnO_2 or Sn compounds as an electrochromic electrode, it is known that SnO_2 is capable of reversible intercalation of an Li ion (see Journal of Electrochemical Society, Vol. 140, No. 5, L81 (1993) and that a film comprising InO_2 doped with 8 mol% of Sn (i.e., ITO) is capable of reversible intercalation of an Li ion (see Solid State Ionics, Vols. 28-30, p. 1733 (1988)). However, the electrode useful in an electrochromic system should be transparent, the active material is used in the form of a thin film formed by, for example, vacuum evaporation, and the electrode usually works at a considerably low current differing from the practical range of batteries. For example, Solid State Ionics, supra, shows a working current of 1 μA to 30 $\mu\text{A}/\text{cm}^2$ as an experimental example.

Known positive electrode active materials include spinel compounds disclosed in JP-B-4-30146 and cobalt oxide disclosed in JP-B-63-59507.

It is possible to combine these positive electrode active materials with an oxide mainly comprising Sn as a negative electrode active material to provide a nonaqueous secondary battery having a high discharge potential, a high capacity, improved charge and discharge cycle characteristics, and increased safety. Yet, the charge and discharge cycle characteristics are still unsatisfactory as described above, and it has been keenly demanded to further improve charge and discharge cycle characteristics.

SUMMARY OF THE INVENTION

55 An object of the present invention is to provide a nonaqueous secondary battery having improved charge and discharge cycle characteristics, a high discharge potential, a high discharge capacity, and increased safety.

The above object of the present invention is accomplished by a nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, in which (1) the negative electrode active material contains at least one compound capable of intercalating and deintercalating lithium mainly comprising

an atom of the group IIIB, IVB (except for Si) or VB of the periodic table, (2) the negative electrode active material mainly comprises an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB (except for Si), and VB of the periodic table, or (4) the negative electrode active material contains at least one compound of the atom of the group IIIB, IVB (except for Si) or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is the X-ray diffraction pattern of compound D-1-A prepared in Synthesis Example D-1.

Fig. 2 is a cross section of a coin battery prepared in Examples, wherein 1 indicates a negative electrode sealing plate, 2 indicates a negative electrode active material mixture pellet, 3 indicates a separator, 4 indicates a positive electrode active material mixture pellet, 5 indicates a collector, 6 indicates a positive electrode case, and 7 indicates a gasket.

Fig. 3 is a cross section of a cylindrical battery prepared in Examples, wherein 8 indicates a positive electrode sheet, 9 indicates a negative electrode sheet, 10 indicates a separator, 11 indicates a battery case, 12 indicates a battery cover, 13 indicates a gasket, and 14 indicates a safety valve.

DETAILED DESCRIPTION OF THE INVENTION

The terminology "negative electrode active material precursor" as used herein is explained below. The inventors have found that SnO having an α -PbO structure, SnO₂ having a rutile structure, and the like do not act by themselves as a negative electrode active material of a secondary battery but change their crystal structure on intercalation of lithium to act as a reversible negative electrode active material. That is, the charge and discharge efficiency of the first cycle is as low as about 80% or 60%. Thus, the starting material, such as α -PbO-structure SnO or rutile-structure SnO₂, namely, a compound before lithium intercalation is called a "negative electrode active material precursor".

The negative electrode active material according to the present invention can be obtained by electrochemically intercalating a lithium ion into, for example, an oxide, an active material precursor. Lithium ion intercalation is conducted until the basic structure of the oxide is changed (for example, until the X-ray diffraction pattern changes) and also until the thus changed basic structure of the Li ion-containing oxide undergoes substantially no change during charging and discharging (for example, the X-ray diffraction pattern does not change substantially). The change in basic structure means change from a certain crystal structure to a different crystal structure or from a crystal structure to an amorphous structure.

Where the compound represented by formulae (I) to (V) of the present invention described in later is used as a negative electrode active material precursor, it was found that intercalation of lithium does not cause reduction of the respective metal (an alloy with lithium). This can be confirmed from the fact that (1) observation under a transmission electron microscope reveals no precipitation of a metal (especially no precipitation of a dendrite), (2) the potential of lithium intercalation/deintercalation via a metal is different from that of the oxide, and (3) the lithium deintercalation loss with respect to lithium intercalation in SnO was about 1 equivalent, which does not agree with a loss of 2 equivalents in the case where metallic tin is generated. Since the potential of an oxide is similar to that of a currently employed calcined carbonaceous compound, it is assumed that the bonding state of lithium is neither mere ionic bonding nor mere metallic bonding, similarly to a calcined carbonaceous compound. Accordingly, the negative electrode active material of the present invention is obviously different from conventional lithium alloys.

It is preferable that the active material precursor which can be used in the present invention is substantially amorphous at the time of battery assembly (before lithium ion intercalation). The term "substantially amorphous" as used herein means that an X-ray diffraction pattern using CuK α rays shows a broad scattering band with peaks between 20° and 40° in terms of 2 θ and may contain diffraction assigned to a crystalline structure.

The maximum intensity of the peaks assigned to the crystalline structure appearing between 2 θ =40° and 70° is preferably not higher than 500 times, still preferably not higher than 100 times, still more preferably not higher than 5 times, the intensity of the peak of the broad scattering band appearing between 2 θ =20° and 40°. It is the most preferred that the pattern exhibits no crystalline diffraction spectrum.

Also, it is preferred that the active material precursor is substantially amorphous at the time of intercalating lithium ion.

In the present invention, either the active material precursor or the active material can be used as a negative electrode. Hereinafter, cases are met in which they are represented as an active material.

The metals of the groups IIIB to VB of the periodic table which can be used in the present invention include B, Al, Ga, In, Tl, Ge, Sn, Pb, P, As, Sb, and Bi, preferably B, Al, Ge, Sn, Pb, P, As, Sb, and Bi, still preferably Al, Ge, Sn, Pb, As, and Sb or B, Al, Ge, Sn, and P.

Still preferred negative electrode active materials are represented by formula (I):



wherein M^1 and M^2 , which are different from each other, each represent at least one of Ge, Sn, Pb, P, B, Al, As, and Sb, preferably at least one of Ge, Sn, Pb, P, B, Al, and Sb, still preferably at least one of Ge, Sn, Pb, P, B, and Al; M^4 represents at least one of O, S, Se, and Te, preferably at least one of O and S, still preferably O; p represents a number exceeding 0 and not exceeding 10, generally from 0.001 to 10, preferably from 0.01 to 5, still preferably from 0.01 to 2; and q represents a number of from 1 to 50, preferably 1 to 26, still preferably 1.02 to 6.

Also, preferred are those of formula (I) in which M^1 and M^2 are different from each other; M^1 represents at least one of Ge, Sn, Pb, Sb, and Bi; M^2 represents at least one atom of the groups IIIB, IVB (except for Si), and VB of the periodic table (exclusive of Ge, Sn, Pb, Sb, and Bi when M^1 represents each of these); p represents a number of from 0.001 to 1; and M^4 and q have the same meanings as defined in formula (I) above.

The valency of M^1 or M^2 in formula (I) is not particularly limited and may be either a single valency or a mixed valency. The M^2 to M^1 ratio may vary continuously within a range of from more than 0 up to 10 molar equivalents. The amount of M^4 , represented by q in formula (I), continuously varies accordingly.

Of the compounds of formula (I), preferred are those in which M^1 is Sn, i.e., compounds represented by formula (II):



wherein M^3 represents at least one of Ge, Pb, P, B, Al, As, and Sb, preferably at least one of Ge, Pb, P, B, Al, and Sb, still preferably at least one of Ge, Pb, P, B, and Al; M^5 represents at least one of O and S, preferably O; p represents a number exceeding 0 and not exceeding 10, generally from 0.001 to 10, preferably from 0.01 to 5, more preferably a number of from 0.01 to 1.5, still preferably from 0.7 to 1.5; and q represents a number of from 1.0 to 50, preferably from 1.0 to 26, still preferably from 1.02 to 6.

Still preferred of the compounds represented by formula (II) are those represented by formula (III):



wherein M^3 is as defined above; r represents a number of exceeding 0 and not exceeding 5.0, generally from 0.01 to 5.0, preferably a number of from 0.01 to 1.5, still preferably from 0.7 to 1.5; and s represents a number of from 1.0 to 26, preferably from 1.02 to 6.

Examples of the compounds represented by formula (II) or (III) are $SnGe_{0.01}O_{1.02}$, $SnPb_{0.01}O_{1.02}$, $SnP_{0.01}O_{1.025}$, $SnB_{0.01}O_{1.015}$, $SnAl_{0.01}O_{1.015}$, $SnGe_{0.01}O_{2.02}$, $SnPb_{0.01}O_{2.02}$, $SnP_{0.01}O_{2.025}$, $SnB_{0.01}O_{2.015}$, $SnGe_{0.05}O_{1.1}$, $SnPb_{0.05}O_{1.1}$, $SnP_{0.05}O_{1.125}$, $SnB_{0.05}O_{1.075}$, $SnGe_{0.05}O_{2.1}$, $SnPb_{0.05}O_{2.1}$, $SnP_{0.05}O_{2.125}$, $SnB_{0.05}O_{2.075}$, $SnGe_{0.1}O_{1.2}$, $SnPb_{0.1}O_{1.2}$, $SnP_{0.1}O_{1.25}$, $SnB_{0.1}O_{1.15}$, $SnGe_{0.1}O_{2.2}$, $SnPb_{0.1}O_{2.2}$, $SnP_{0.1}O_{2.25}$, $SnB_{0.1}O_{2.15}$, $SnGe_{0.2}O_{1.4}$, $SnPb_{0.2}O_{1.4}$, $SnP_{0.2}O_{1.5}$, $SnB_{0.2}O_{1.3}$, $SnGe_{0.2}O_{2.4}$, $SnPb_{0.2}O_{2.4}$, $SnP_{0.2}O_{2.5}$, $SnB_{0.2}O_{2.3}$, $SnGe_{0.3}O_{1.6}$, $SnPb_{0.3}O_{1.6}$, $SnP_{0.3}O_{1.75}$, $SnB_{0.3}O_{1.45}$, $SnGe_{0.3}O_{2.6}$, $SnPb_{0.3}O_{2.6}$, $SnP_{0.3}O_{2.75}$, $SnB_{0.3}O_{2.45}$, $SnGe_{0.7}O_{2.4}$, $SnPb_{0.7}O_{2.4}$, $SnP_{0.7}O_{2.75}$, $SnB_{0.7}O_{2.05}$, $SnGe_{0.8}O_{2.6}$, $SnPb_{0.8}O_{2.6}$, $SnP_{0.8}O_3$, $SnB_{0.8}O_{2.2}$, $SnGeO_3$, $SnPbO_3$, $SnPO_{3.5}$, $SnBO_{2.5}$, $SnGe_{1.2}O_{3.4}$, $SnPb_{1.2}O_{3.4}$, $SnP_{1.2}O_4$, $SnB_{1.2}O_{2.8}$, $SnGe_{1.5}O_4$, $SnPb_{1.5}O_4$, $SnP_{1.5}O_{4.75}$, $SnB_{1.5}O_{3.25}$, $SnGe_2O_5$, $SnPb_2O_5$, SnP_2O_6 , SnB_2O_4 , $SnGe_2O_6$, $SnPb_2O_6$, SnP_2O_7 , SnB_2O_5 , $SnSi_3S_3$, $SnPS_{3.5}$, $SnPSe_{3.5}$, $SnPTe_{3.5}$, $SnBS_{2.5}$, $SnBSe_{2.5}$, $SnBTe_{2.5}$, $SnP_{0.8}O_3$, $SnB_{0.8}O_{2.2}$.

The valency of Sn and M^3 in formula (II) or (III) is not particularly limited and may be a single valency or a mixed valency. The ratio of M^3 to Sn in the compound of formula (II) may vary continuously within a range of from 0.01 to 10 molar equivalents. Accordingly, the amount of M^5 , represented by q in formula (II), varies continuously. Similarly, the ratio of M^3 to Sn in the compound of formula (III) may vary continuously within a range of from 0.01 to 5.0 molar equivalents. Accordingly, the amount of oxygen, represented by s in formula (III), varies continuously.

Additional examples of the compounds represented by formulae (I) to (III) are shown below.

$SnAl_{0.1}O_{3.65}$, $SnAl_{0.3}O_{3.95}$, $SnP_{0.8}Al_{0.1}O_{3.15}$, $SnP_{0.8}Al_{0.3}O_{2.45}$, $SnP_{0.5}Al_{0.1}O_{2.4}$, $SnP_{0.5}Al_{0.3}O_{2.7}$, $SnGe_{0.2}Pb_{0.1}O_{2.6}$, $SnPb_{0.2}Ge_{0.1}O_{2.6}$, $SnP_{0.9}Ge_{0.1}O_{3.45}$, $SnP_{0.8}Ge_{0.2}O_{3.4}$, $SnP_{0.5}Ge_{0.5}O_{3.25}$, $SnP_{0.9}Pb_{0.1}O_{3.45}$, $SnP_{0.8}Pb_{0.2}O_{3.4}$, $SnP_{0.5}Pb_{0.5}O_{3.25}$, $SnGe_{0.9}P_{0.1}O_{3.05}$, $SnGe_{0.8}P_{0.2}O_{3.1}$, $SnPb_{0.9}P_{0.1}O_{3.05}$, $SnPb_{0.8}P_{0.2}O_{3.1}$, $SnP_{0.8}Ge_{0.1}Pb_{0.1}O_{3.4}$, $SnB_{0.9}Ge_{0.1}O_{2.55}$, $SnB_{0.8}Ge_{0.2}O_{2.6}$, $SnB_{0.5}Ge_{0.5}O_{2.75}$, $SnB_{0.9}Pb_{0.1}O_{2.55}$, $SnB_{0.8}Pb_{0.2}O_{2.6}$, $SnB_{0.5}Pb_{0.5}O_{2.75}$, $SnGe_{0.9}B_{0.1}O_{2.95}$, $SnGe_{0.8}B_{0.2}O_{2.9}$, $SnPb_{0.9}B_{0.1}O_{2.95}$, $SnPb_{0.8}B_{0.2}O_{2.9}$, $SnB_{0.8}Ge_{0.1}Pb_{0.1}O_{2.6}$, $SnAl_{0.1}O_{3.65}$, $SnAl_{0.3}O_{3.95}$, $SnP_{0.8}Al_{0.1}O_{3.15}$, $SnP_{0.8}Al_{0.3}O_{2.45}$, $SnP_{0.5}Al_{0.1}O_{2.4}$, $SnP_{0.5}Al_{0.3}O_{2.7}$, $PbGe_{0.01}O_{1.02}$, $PbGe_{0.01}O_{2.02}$, $PbP_{0.01}O_{1.025}$, $PbB_{0.01}O_{1.015}$, $PbP_{0.01}O_{2.025}$, $PbGe_{0.01}O_{2.015}$, $PbGe_{0.05}O_{1.1}$, $PbSi_{0.05}O_{2.1}$, $PbGe_{0.05}O_{2.1}$, $PbP_{0.05}O_{1.125}$, $PbB_{0.05}O_{1.075}$, $PbP_{0.05}O_{2.125}$, $PbB_{0.05}O_{2.075}$, $PbGe_{0.1}O_{2.2}$, $PbSi_{0.1}O_{1.2}$, $PbGe_{0.1}O_{1.2}$, $PbP_{0.1}O_{2.25}$, $PbB_{0.1}O_{2.15}$, $PbP_{0.1}O_{1.25}$, $PbB_{0.1}O_{1.15}$, $PbGe_{0.2}O_{2.4}$, $PbGe_{0.2}O_{1.4}$, $PbP_{0.2}O_{2.5}$, $PbB_{0.2}O_{2.3}$, $PbP_{0.2}O_{1.5}$, $PbB_{0.2}O_{1.3}$, $PbGe_{0.3}O_{2.6}$, $PbSi_{0.3}O_{1.6}$, $PbGe_{0.3}O_{1.6}$, $PbP_{0.3}O_{2.75}$, $PbB_{0.3}O_{2.45}$, $PbP_{0.3}O_{1.75}$, $PbB_{0.3}O_{1.45}$, $PbP_{0.2}Ge_{0.1}O_{2.7}$, $PbGe_{0.2}P_{0.1}O_{2.65}$, $PbB_{0.2}Ge_{0.1}O_{2.5}$, $PbGe_{0.2}B_{0.1}O_{2.55}$, $PbGe_{0.7}O_{2.4}$, $PbP_{0.7}O_{2.75}$, $PbB_{0.7}O_{2.05}$, $PbGe_{0.8}O_{2.6}$, $PbP_{0.8}O_3$, $PbB_{0.8}O_{2.2}$, $PbSiO_3$, $PbGeO_3$, $PbPO_{3.5}$, $PbBO_{2.5}$, $PbP_{0.9}Ge_{0.1}O_{3.45}$, $PbP_{0.8}Ge_{0.2}O_{3.4}$.

PbP_{0.5}Ge_{0.5}O_{3.25}, PbB_{0.9}Ge_{0.1}O_{2.65}, PbB_{0.8}Ge_{0.2}O_{2.6}, PbB_{0.5}Ge_{0.5}O_{2.75}, PbGe_{0.9}P_{0.1}O_{3.05}, PbGe_{0.8}P_{0.2}O_{3.1}, PbGe_{0.9}B_{0.1}O_{2.95}, PbGe_{0.8}B_{0.2}O_{2.9}, PbGe_{1.5}O₄, PbP_{1.5}O_{4.75}, PbB_{1.5}O_{3.25}, PbGe₂O₅, PbGe₂O₆, PbP₂O₇, PbB₂O₅, GeP_{0.01}O_{1.025}, GeP_{0.01}O_{2.025}, GeP_{0.05}O_{1.125}, GeP_{0.05}O_{2.125}, GeP_{0.1}O_{1.25}, GeP_{0.1}O_{2.25}, GeP_{0.2}O_{1.5}, GeP_{0.2}O_{2.5}, GeP_{0.3}O_{1.75}, GeP_{0.3}O_{2.75}, GeP_{0.5}O_{2.25}, GeP_{0.5}O_{3.25}, GeP_{0.7}O_{2.75}, GeP_{0.7}O_{3.75}, GePO_{3.5}, GePO_{4.5}, GeP_{1.5}O_{4.75}, GeP_{1.5}O_{5.75}, GeB_{0.01}O_{1.015}, GeB_{0.01}O_{2.015}, GeB_{0.05}O_{1.075}, GeB_{0.05}O_{2.075}, GeB_{0.1}O_{1.15}, GeB_{0.1}O_{2.15}, GeB_{0.2}O_{1.3}, GeB_{0.2}O_{2.3}, GeB_{0.3}O_{1.45}, GeB_{0.3}O_{2.45}, GeB_{0.5}O_{1.75}, GeB_{0.5}O_{2.75}, GeB_{0.7}O_{2.05}, GeB_{0.7}O_{3.05}, GeBO_{2.5}, GeBO_{3.5}, GeB_{1.5}O_{3.25} and GeB_{1.5}O_{4.25}.

The use of any of the compounds represented by formulae (I) to (III) as a main negative electrode active material affords a nonaqueous secondary battery having excellent charge and discharge cycle characteristics, a high discharge potential, a high capacity and high safety.

The pronouncedly excellent effects of the present invention come from the use of a compound containing Sn in which Sn is present with divalency. The valency of Sn can be determined through chemical titration, for example, according to the method described in Physics and Chemistry of Glasses, Vol. 8, No. 4, p. 165 (1967). It is also decided from the Knight shift in the solid nuclear magnetic resonance spectrum of Sn. For example, in broad-line NMR measurement, metallic Sn (zero valent Sn) shows a peak in an extremely low magnetic field in the vicinity of 7000 ppm with reference to Sn(CH₃)₄, whereas the peak of SnO (divalent Sn) appears around 100 ppm, and that of SnO₂ (tetravalent Sn) appears around -600 ppm. Like this, the Knight shift largely depends on the valency of Sn, the center metal, with the ligands being the same. The valency can thus be determined by the peak position obtained by ¹¹⁹Sn-NMR analysis.

The negative electrode active material of the present invention may contain various compounds, such as compounds of the group IA elements (e.g., Li, Na, K, Rb, and Cs), transition metals (e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, lanthanoid metals, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg), the group IIA elements (e.g., Be, Mg, Ca, Sr, Ba), and the group VIIIB elements (e.g., F, Cl, Br, I). Further, it may also contain dopants of various compounds (e.g., compounds of Sb, In, Nb) for improving electrical conductivity. The addition amount thereof is preferably 0 to 20 mol%.

The compounds of formulae (I) to (III) can be synthesized by either a calcination method or a solution method.

For instance, the calcination method is conducted by calcining a mixed compound of M¹ compound and M² compound (where M¹ and M², which are different from each other, each represent Ge, Sn, Pb, P, B, Al, As, Sb).

The tin compounds include SnO, SnO₂, Sn₂O₃, Sn₃O₄, Sn₇O₁₃ · H₂O, Sn₈O₁₅, stannous hydroxide, stannic oxyhydroxide, stannic acid, stannous oxalate, stannous phosphate, orthostannic acid, metastannic acid, parastannic acid, stannous fluoride, stannic fluoride, stannous chloride, stannic chloride, stannous bromide, stannic bromide, stannous iodide, stannic iodide, tin selenide, tin telluride, stannous pyrophosphate, tin phosphite, stannous sulfate, stannic sulfate.

The germanium compounds include GeO₂, GeO, germanium tetrachloride, and alkoxy germanium compounds such as germanium tetramethoxide and germanium tetraethoxide.

The lead compounds include PbO₂, PbO, Pb₂O₃, Pb₃O₄, PbCl₂, lead chlorate, lead perchlorate, lead nitrate, lead carbonate, lead formate, lead acetate, lead tetraacetate, lead tartrate, lead diethoxide, lead di(isopropoxide).

The phosphorus compound includes phosphorus pentoxide, phosphorus oxychloride, phosphorous pentachloride, phosphorus trichloride, phosphorous tribromide, trimethyl phosphate, triethyl phosphate, tripropyl phosphate, stannous pyrophosphate, and boron phosphate.

The boron compound includes boron sesquioxide, boron trichloride, boron tribromide, boron carbide, boric acid, trimethyl borate, triethyl borate, tripropyl borate, tributyl borate, boron phosphide, and boron phosphate.

The aluminum compound includes aluminum oxide (α-alumina or β-alumina), aluminum silicate, aluminum triisopropoxide, aluminum tellurite, aluminum chloride, aluminum boride, aluminum phosphide, aluminum phosphate, aluminum lactate, aluminum borate, aluminum sulfide, and aluminum sulfate.

The antimony compound includes antimony tribromide, antimony trichloride, diantimony trioxide, and triphenylantimony.

Calcination is carried out preferably at a rate of temperature rise of 4° to 2000°C/min, still preferably 6° to 2000°C/min, most preferably 10° to 2000°C/min; at a calcination temperature of 250° to 1500°C, still preferably 350° to 1500°C, most preferably 500° to 1500°C; for a period of 0.01 to 100 hours, still preferably 0.5 to 70 hours, most preferably 1 to 20 hours. After calcination, the system is cooled at a rate of temperature drop of 2° to 10⁷°C/min, still preferably 4° to 10⁷°C/min, still more preferably 6° to 10⁷°C/min, most preferably 10° to 10⁷°C/min.

The term "rate of temperature rise" as used herein means an average rate of temperature rise from 50% calcination temperature (°C) up to 80% calcination temperature (°C), and the term "rate of temperature drop" as used herein means an average rate of temperature drop from 80% calcination temperature (°C) to 50% calcination temperature (°C).

Cooling of the calcined product may be effected either within a calcining furnace or out of the furnace, for example, by pouring the product into water. Super-quenching methods described in Ceramics Processing, p. 217, Gihodo (1987), such as a gun method, a Hammer-Anvil method, a slap method, a gas atomizing method, a plasma spray method, a

centrifugal quenching method, and a melt drag method, can also be used. Further, cooling may be conducted by a single roller method or a twin-roller method described in New Glass Handbook, p. 172, Maruzen (1991). Where the material melts during calcination, the calcined product may be withdrawn continuously while feeding the raw materials. The molten liquid is preferably stirred during calcination.

The calcining atmosphere preferably has an oxygen content of not more than 100% by volume, preferably not more than 20% by volume, more preferably not more than 5% by volume. An inert gas atmosphere is still preferred. Inert gas includes nitrogen, argon, helium, krypton, and xenon.

The compound of formulae (I) to (V) preferably has an average particle size of from 0.1 to 60 μm . The calcined product can be ground to size by means of well-known grinding machines or classifiers, such as a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planetary ball mill, a spinning air flow type jet mill, and a sieve. If necessary, wet grinding using water or an organic solvent, such as methanol, may be conducted. The grinds are preferably classified to obtain a desired particle size either by dry or wet classification by means of a sieve, an air classifier, etc.

The positive electrode active material which can be used in the present invention may be a transition metal oxide capable of reversibly intercalating and deintercalating a lithium ion but is preferably a lithium-containing transition metal oxide.

Lithium-containing transition metal oxides which can be used as a positive electrode active material include, for preference, lithium-containing oxides of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo or W. The oxide may contain other alkali metals (the group IA and IIA elements) in addition to Li and/or other elements such as Al, Ga, In, Ge, Sn, Pb, Sb, Bi, Si, P, B, etc. The ratio of these additional elements is preferably up to 30 mol%, still preferably up to 10 mol%, based on the transition metal.

Preferred of the Li-containing transition metal oxides as a positive electrode active material are those prepared from a mixture of a lithium compound and at least one compound of a transition metal selected from Ti, V, Cr, Mn, Fe, Co, Ni, Mo, and W at a lithium compound/total transition metal compounds molar ratio of 0.3 to 2.2.

Still preferred are those prepared from a mixture of a lithium compound and at least one compound of a transition metal selected from V, Cr, Mn, Fe, Co, and Ni at a lithium compound/total transition metal compounds molar ratio of from 0.3 to 2.2.

The most preferred are those represented by formula Li_xQO_y (Q represents at least one transition metal selected from Co, Mn, Ni, V, and Fe; x is from 0.2 to 1.2; and y is from 1.4 to 3). Q may contain, in addition to a transition metal, other metals, such as Al, Ga, In, Ge, Sn, Pb, Sb, Bi, Si, P, B, etc. The ratio of the other metals is preferably up to 30 mol% based on the total transition metals.

Suitable examples of the lithium-containing metal oxide positive electrode active material which can be preferably used in the present invention are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{Fe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Co}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Ni}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{V}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Fe}_{2-c}\text{O}_4$, a mixture of $\text{Li}_x\text{Mn}_2\text{O}_4$ and MnO_2 , a mixture of $\text{Li}_{2x}\text{MnO}_3$ and MnO_2 , a mixture of $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_{2x}\text{MnO}_3$, and MnO_2 (wherein $x = 0.2$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.8$ to 0.98 ; $c = 1.6$ to 1.96 ; and $z = 2.01$ to 5).

Preferred examples of the lithium-containing metal oxide positive electrode active materials are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$, $\text{Li}_x\text{Co}_b\text{Fe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Co}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{Ni}_{2-c}\text{O}_4$, $\text{Li}_x\text{Mn}_c\text{V}_{2-c}\text{O}_4$, and $\text{Li}_x\text{Mn}_c\text{Fe}_{2-c}\text{O}_4$ (wherein $x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.8$ to 0.98 ; $c = 1.6$ to 1.96 ; $z = 2.01$ to 2.3).

Still preferred of the lithium-containing metal oxide positive electrode active materials are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, and $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ (wherein $x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.01$ to 2.3).

The most preferred are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, and $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ (wherein $x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3).

The value x in the above formulae is the value before commencement of charging and discharging and varies with a charge and a discharge.

According to another embodiment of the present invention, a spinel type manganese-containing oxide is used as a positive electrode active material. Spinel type oxides have a spinel structure represented by formula $\text{A}(\text{B}_2)\text{O}_4$, in which the oxygen anions are aligned in cubic closest packing and occupy part of the faces and apexes of a tetrahedron and an octahedron. The unit cell is composed of 8 molecules, and oxygen occupies 32e positions in the $\text{Fd}3\text{m}$ space. The unit cells occupy the lattice spacing of 64 octahedrons at three crystallographically non-equivalent positions, 8a, 8b, and 48f. In this spinel structure, cations B are positioned at the lattice spacing sites of the 16d octahedrons (the vacant octahedron site is 16c), and cations A are positioned at the lattice spacing sites of the 8a tetrahedrons. Each 8a octahedron shares the face with the adjoining 4 vacant 16c octahedrons thereby to provide passageways through which cations A diffuse (e.g., $8a \rightarrow 16c \rightarrow 8a \rightarrow 16c$). On the other hand, each 8b tetrahedron shares the face with the 16d octahedron formed of cations B, resulting in energy disadvantage to cations' occupation. The 48f tetrahedron shares the face with both the 16d and 16c octahedrons. According to the distribution of cations A, $\text{A}(\text{B}_2)\text{O}_4$ is called a normal spinel structure, and $\text{B}(\text{AB})\text{O}_4$ is called an inverse-spinel structure. $\text{A}_x\text{B}_y(\text{A}_{1-x}\text{B}_{1-y})\text{O}_4$, an intermediate structure between a normal

spinel and an inverse-spinel, is also called a spinel.

Manganese oxides having a normal spinel structure typically include LiMn_2O_4 , which serves as a positive electrode active material. In this structure, a half of the Mn cations are trivalent, with the another half being tetravalent. $\lambda\text{-MnO}_2$, also known as an active material, is regarded to have a spinel structure with defects, derived by removing lithium from LiMn_2O_4 , in which all the Mn cations are tetravalent, as described in U.S. Patent 4,246,253. The manganese oxide positive electrode active materials which can be used in the present invention include all of those having a normal spinel structure, those having an inverse-spinel structure, those having a defect-free structure, and those having a non-stoichiometrical spinel structure with defects.

Suitable Li-containing manganese oxides having a spinel structure which can be used in the present invention include those represented by general formula $\text{Li}_{1+x}[\text{Mn}_{2-y}]_4\text{O}_4$ ($0 < x < 1.7$; $0 \leq y < 0.7$). Such compounds include $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (or $\text{Li}[\text{Li}_{1/3}\text{Mn}_{5/3}]\text{O}_4$). In addition, the following compounds are also included under the scope covered by the above general formula (structural formulae include those represented by multiplying the general formula by an integer or a decimal):

$\text{Li}_4\text{Mn}_4\text{O}_9$, LiMnO_2 (or $\text{Li}_2\text{Mn}_2\text{O}_4$), Li_2MnO_3 , $\text{Li}_5\text{Mn}_4\text{O}_9$, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$

Suitable Li-containing manganese oxides having a spinel structure which can be used as a positive electrode active material in the present invention further include those represented by general formula $\text{Li}_{1-x}[\text{Mn}_{2-y}]_4\text{O}_4$ ($0 < x < 1.0$; $0 \leq y < 0.5$). Preferred of them are those represented by general formula $\text{Li}_{1-x}[\text{Mn}_{2-y}]_4\text{O}_4$ ($0.20 < x < 1.0$; $0 < y < 0.2$), such as $\text{Li}_2\text{Mn}_5\text{O}_{11}$ (or $\text{Li}_{1-x}[\text{Mn}_{2-y}]_4\text{O}_4$ ($x = 0.273$; $y = 0.182$)), which is a non-stoichiometrical spinel compound disclosed in JP-A-4-240117; and those represented by general formula $\text{Li}_{1-x}[\text{Mn}_{2-y}]_4\text{O}_4$ ($0 < x \leq 0.20$; $0 < y < 0.4$), such as $\text{Li}_2\text{Mn}_4\text{O}_9$. In addition, the following compounds are also included under the scope covered by the above formula $\text{Li}_{1-x}[\text{Mn}_{2-y}]_4\text{O}_4$ (structural formulae include those represented by multiplying the general formula by an integer or a decimal):

$\text{Li}_4\text{Mn}_{16.5}\text{O}_{35}$, $\text{Li}_2\text{Mn}_{7.5}\text{O}_{16}$, and $\text{Li}_{0.7}\text{MnO}_4$

The above-mentioned spinel type manganese oxides as a positive electrode active material can be obtained by reacting a lithium salt and a manganese salt or a manganese oxide in a solid phase at a high temperature according to a known method. In using lithium carbonate and manganese dioxide as starting materials, calcination is carried out at 350° to 900°C , preferably 350° to 500°C , for 8 to 48 hours. In using lithium nitrate having a low melting point (261°C) as a lithium salt, calcination is carried out at 300° to 900°C , preferably 300° to 500°C . Manganese oxides to be used include $\lambda\text{-MnO}_2$, electrolytically prepared MnO_2 (EMD), chemically prepared MnO_2 (CMD), and a mixture thereof. Lithium-manganese double oxides (e.g., $\text{Li}_2\text{Mn}_4\text{O}_9$) may also be used as a lithium material. In this case, the Li-Mn double oxide is mixed with a manganese material, e.g., manganese dioxide, and calcined at 350° to 500°C .

The spinel type manganese oxide may be doped with one or more of other transition metal elements, typical elements, and rare earth elements to form a compound oxide. Preferred dopants are transition metal elements, such as Co, Ni, Ti, V, Zr, Nb, Mo, W, and Fe.

The positive electrode active materials which can be used in the present invention also include manganese oxide compounds having a hollandite skeleton structure as disclosed in JP-A-4-270125, which are regarded as having the above-described general formulae with part or most part (e.g., 95% or more) of Li cations thereof being substituted with other cations, e.g., H, K, Na, and ammonium ions. Hollandite type compounds in which Li cations are substituted with H can easily be obtained by, for example, treating an Li-Mg double oxide represented by the above general formula with an acid at a high temperature to remove Li.

The positive electrode active materials can be synthesized by mixing a lithium compound and a transition metal compound, followed by calcination or by reacting these materials in a solution. The former calcination method is preferred.

Calcination is carried out at a calcination temperature selected from the range in which at least part of the mixed compounds may be decomposed and melted, for example, from 250° to 2000°C , preferably from 350° to 1500°C , for 1 to 72 hours, preferably 2 to 20 hours. Prior to calcination, the mixture is preferably pre-calcined at 250° to 900°C . Mixing of the raw materials may be either dry blending or wet blending. If desired, calcination may be followed by annealing at 200° to 900°C .

The calcination atmosphere is not limited and may be an oxidizing atmosphere or a reducing atmosphere. For example, calcination can be performed in air, a prepared gas having an arbitrary oxygen concentration, hydrogen, carbon monoxide, nitrogen, argon, helium, krypton, xenon, or carbon dioxide.

In the synthesis of positive electrode active materials, chemical intercalation of a lithium ion into a transition metal oxide is preferably achieved by reacting metallic lithium, a lithium alloy or butyl lithium with the transition metal oxide.

While not limiting, the positive electrode active material to be used in the present invention preferably has an average particle size of from 0.1 to 50 μm and a BET specific surface area of from 0.01 to 50 m^2/g . An aqueous solution

(supernatant liquid) of 5 g of a positive electrode active material in 100 ml of distilled water preferably has a pH of 7 to 12.

The resulting positive electrode active material can be ground to size by means of well-known grinding machines or classifiers, such as a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planetary ball mill, a spinning air flow type jet mill, and a sieve.

If desired, the positive electrode active material obtained by calcination may be washed with water, an aqueous acid solution, an aqueous alkali solution or an organic solvent before use.

A preferred combination of a negative electrode active material and a positive electrode active material is a combination of a compound of formula (I) as a negative electrode active material and Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, or $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ ($x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3) as a positive electrode active material, still preferably a combination of a compound of formula (III) and Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, or $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ ($x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3) as a positive electrode active material, most preferably a combination of a compound of formula (IV) as a negative electrode active material and Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Co}_a\text{Ni}_{1-a}\text{O}_2$, Li_xMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, or $\text{Li}_x\text{Co}_b\text{V}_{1-b}\text{O}_2$ ($x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.9$ to 0.98 ; and $z = 2.02$ to 2.3) as a positive electrode active material.

Further, preferred is a combination of a compound of formula (I) as a negative electrode active material and $\text{Li}_4\text{Mn}_4\text{O}_9$, LiMnO_2 , $\text{Li}_2\text{Mn}_2\text{O}_4$, Li_2MnO_3 , $\text{Li}_5\text{Mn}_4\text{O}_9$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, $\text{LiMn}_{16.5}\text{O}_{35}$, $\text{Li}_2\text{Mn}_{7.5}\text{O}_{16}$ or $\text{Li}_{0.7}\text{Mn}_2\text{O}_4$.

Such combinations of active materials afford a nonaqueous secondary battery having excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

Lithium is intercalated into a compound represented by any of formulas (I) to (V) in an amount of from 1 to 20 equivalents, preferably from 3 to 10 equivalents.

The ratio of a positive electrode active material to a negative electrode active material is decided according to the above-mentioned equivalent amount. It is preferable to use a positive electrode active material in an amount based on the calculated ratio multiplied by 0.5 to 2. Where any other substance than a positive electrode active material, e.g., metallic lithium, a lithium alloy or butyl lithium, is used as a lithium source, the amount of a positive electrode active material to be used is decided in conformity with the equivalent amount of deintercalated lithium of the negative electrode active material. In this case, too, the ratio based on the equivalent amount is preferably multiplied by 0.5 to 2.

Negative electrode active materials which may be used in combination with the negative electrode active material of the present invention include metallic lithium, lithium alloys (e.g., alloys with Al, Al-Mn, Al-Mg, Al-Sn, Al-In or Al-Cd), and calcined carbonaceous compounds capable of intercalating and deintercalating a lithium ion or metallic lithium.

The purpose of the combined use of metallic lithium or a lithium alloy is to intercalate lithium into a compound mainly comprising an oxide of formula (I) to (V) within a cell but not to utilize the dissolution-precipitation reaction of metallic lithium, etc. as an electrode reaction.

An electrode material mixture which can be used in the present invention comprises the above-described active material, a conducting agent, a binder, a filler, and so forth.

The conducting agent may be any electron-conducting material which undergoes no chemical change in an assembled battery. Suitable conducting agents include natural graphite (scale graphite, flake graphite, lumpy graphite, etc.), artificial graphite, carbon black, acetylene black, Ketjen black, carbon fiber, metal powders (e.g., copper, nickel, aluminum or silver powder), metallic fibers, polyphenylene derivatives, and mixtures of two or more thereof. A combination of graphite and acetylene black is particularly preferred.

The conducting agent is preferably used in an amount of from 1 to 50% by weight, still preferably from 2 to 30% by weight, based on the total weight of the active material mixture. Carbon or graphite is preferably used in an amount of from 2 to 15% by weight.

The binder includes polysaccharides, thermoplastic resins, and rubbery polymers; such as starch, polyvinyl alcohol, carboxymethyl cellulose, hydroxypropyl cellulose, regenerated cellulose, diacetyl cellulose, polyvinyl chloride, polyvinyl pyrrolidone, tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, ethylene-propylene-diene terpolymers (EPDM), sulfonated EPDM, styrene-butadiene rubbers, polybutadiene, fluorine rubbers, polyethylene oxide, and mixtures of two or more thereof. In using a compound having a functional group reactive with lithium, such as a polysaccharide, it is preferable to deactivate the functional group by addition of a compound having an isocyanate group. The binder is used in an amount of 1 to 50% by weight, preferably 2 to 30% by weight, based on the total weight of the active material mixture.

In particular, polymers having a decomposition temperature of not lower than 300°C are preferred as a binder for the negative electrode active material of the present invention. Such polymers include polyethylene, polypropylene, epoxy resins, polyester resins, and fluorine resins, with fluorine resins being preferred. The term "fluorine resin" is used herein as a general term for polymers having a carbon-fluorine bond in the molecule thereof as specified in JIS K6900 "Glossary of Terms Used in Plastic Industry".

Suitable examples of the fluorine resins are shown below.

- (A-1) Polytetrafluoroethylene (PTFE)
- (A-2) Polyvinylidene fluoride (PVDF)
- (A-3) Tetrafluoroethylene-hexafluoropropylene copolymer (FEP)
- (A-4) Tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA)
- (A-5) Vinylidene fluoride-hexafluoropropylene copolymer
- (A-6) Vinylidene fluoride-chlorotrifluoroethylene copolymer
- (A-7) Ethylene-tetrafluoroethylene copolymer (ETFE resin)
- (A-8) Polychlorotrifluoroethylene (PCTFE)
- (A-9) Vinylidene fluoride-pentafluoropropylene copolymer
- (A-10) Propylene-tetrafluoroethylene copolymer
- (A-11) Ethylene-chlorotrifluoroethylene copolymer (ECTFE)
- (A-12) Vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene copolymer
- (A-13) Vinylidene fluoride-perfluoromethyl vinyl ether-tetrafluoroethylene copolymer

Copolymer resins comprising another ethylenically unsaturated monomer in addition to the above-mentioned monomers are also useful. Specific but non-limiting examples of copolymerizable unsaturated monomers include acrylic esters, methacrylic esters, vinyl acetate, acrylonitrile, acrylic acid, methacrylic acid, maleic anhydride, butadiene, styrene, N-vinylpyrrolidone, N-vinylpyridine, glycidyl methacrylate, hydroxyethyl methacrylate, and methyl vinyl ether.

The binder resins can be obtained by any of solution polymerization, emulsion polymerization, suspension polymerization, and gaseous phase polymerization, and the polymer may be any of random polymers, graft polymers, and block polymers.

The above-mentioned binder resin may be used in combination with one or more other polymers, such as carboxymethyl cellulose, sodium polyacrylate, hydroxyethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide, and alginic acid.

The binder is preferably used in an amount of from 0.5 to 30% by weight based on the negative electrode active material.

The filler to be used in the present invention is not particularly limited as long as it is a fibrous material undergoing no chemical change in an assembled battery. Suitable fillers include fibers of polyolefins (e.g., polypropylene or polyethylene), glass fiber, and carbon fiber. While not limiting, the filler is preferably used in an amount of up to 30% by weight based on the total weight of the active material mixture.

The nonaqueous electrolytic solution which can be used in the nonaqueous secondary battery of the present invention consists of at least one organic solvent and at least one lithium salt soluble in the solvent. Suitable organic solvents include aprotic solvents, such as propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, γ -butyrolactone, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, formamide, dimethylformamide, dioxolane, acetonitrile, nitromethane, methyl formate, methyl acetate, methyl propionate, ethyl propionate, phosphoric triesters, trimethoxymethane, dioxolane derivatives, sulfolane, 3-methyl-2-oxazolidinone, propylene carbonate derivatives, tetrahydrofuran derivatives, ethyl ether, and 1,3-propanesultone. These solvents may be used either individually or in combination of two or more thereof. Suitable lithium salts soluble in these solvents include LiClO_4 , LiBF_6 , LiPF_6 , LiCF_3SO_3 , LiCF_3CO_2 , LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, lower aliphatic lithium carboxylates, LiAlCl_4 , LiCl , LiBr , LiI , chloroborane lithium, and lithium tetraphenylborate. These lithium salts may be used either individually or in combination of two or more thereof. In particular, a solution of LiCF_3SO_3 , LiClO_4 , LiBF_4 and/or LiPF_6 in a mixed solvent of propylene carbonate or ethylene carbonate and 1,2-dimethoxyethane and/or diethyl carbonate is a preferred electrolytic solution.

The amount of the electrolytic solution to be used in a battery is not particularly limited and can be selected according to the amounts of the positive and negative electrode active materials or the size of the battery.

The concentration of the supporting electrolyte is preferably from 0.2 to 3 mols per liter of the electrolytic solution.

In addition to electrolytic solutions, inorganic or organic solid electrolytes may also be employed.

Examples of suitable inorganic solid electrolytes include a lithium nitride, a lithium halide, and a lithium oxyacid salt. Among them preferred are Li_3N , LiI , Li_5NI_2 , $\text{Li}_3\text{N-LiI-LiOH}$, LiSiO_4 , $\text{LiSiO}_4\text{-LiI-LiOH}$, $x\text{Li}_3\text{PO}_4\text{-(1-x)Li}_4\text{SiO}_4$, Li_2SiS_3 , and phosphorus sulfide compounds.

Examples of suitable organic solid electrolytes include polyethylene oxide derivatives or polymers containing the same (see JP-A-63-135447), polypropylene oxide derivatives or polymers containing the same, polymers containing an ionizing group (see JP-A-62-254302, JP-A-62-254303, and JP-A-63-193954), a mixture of a polymer containing an ionizing group and the above-mentioned aprotic electrolytic solution (see U.S. Patents 4,792,504 and 4,830,939, JP-A-62-22375, JP-A-62-22376, JP-A-63-22375, JP-A-63-22776, and JP-A-1-95117), and phosphoric ester polymers (see JP-A-61-256573). A combination of polyacrylonitrile and an electrolytic solution (see JP-A-62-278774) and a combination of an organic solid electrolyte and an inorganic solid electrolyte (see JP-A-60-1768) are also known.

As a separator, an insulating thin film having high ion permeability and prescribed mechanical strength is used. A

sheet or nonwoven fabric made of an olefin polymer (e.g., polypropylene), glass fiber or polyethylene is usually employed for their organic solvent resistance and hydrophobic properties. The pore size of the separator is selected from the range generally used for batteries, e.g., from 0.01 to 10 μm . The thickness of the separator is selected from the range generally used for batteries, e.g., from 5 to 300 μm .

For the purpose of improving charge and discharge characteristics, the electrolytic solution may contain other compounds, such as pyridine (see JP-A-49-108525), triethyl phosphite (see JP-A-47-4376), triethanolamine (see JP-A-52-72425), a cyclic ether (see JP-A-57-152684), ethylenediamine (see JP-A-58-87777), n-glyme (see JP-A-58-87778), hexaphosphoric acid triamide (see JP-A-58-87779), a nitrobenzene derivative (see JP-A-58-214281), sulfur (see JP-A-59-8280), a quinoneimine dye (see JP-A-59-68184), an N-substituted oxazolidinone and an N,N'-substituted imidazolidinone (see JP-A-59-154778), an ethylene glycol dialkyl ether (see JP-A-59-205167), a quaternary ammonium salt (see JP-A-60-30065), polyethylene glycol (see JP-A-60-41773), pyrrole (see JP-A-60-79677), 2-methoxyethanol (see JP-A-60-89075), AlCl_3 (see JP-A-61-88466), a monomer providing a conductive polymeric active material (see JP-A-61-161673), triethylenephosphoramidate (see JP-A-61-208758), a trialkylphosphine (JP-A-62-80976), morpholine (see JP-A-62-80977), an aryl compound having a carbonyl group (see JP-A-62-86673), hexamethylphosphoric triamide and a 4-alkylmorpholine (see JP-A-62-217575), a bicyclic tertiary amine (see JP-A-62-217578), an oil (see JP-A-62-287580), a quaternary phosphonium salt (see JP-A-63-121268), and a tertiary sulfonium salt (see JP-A-63-121269).

In order to make the electrolytic solution incombustible, a halogen-containing solvent, such as carbon tetrachloride or trifluorochloroethylene, may be added to the electrolytic solution (see JP-A-48-36632). In order to make the electrolytic solution resistant to high-temperature preservation, carbonic acid gas may be incorporated thereto (see JP-A-59-134567).

The positive or negative electrode active material mixture may contain an electrolytic solution or an electrolyte. For example, it is known to add the above-mentioned ion-conductive polymer or nitromethane (see JP-A-48-36633) or an electrolytic solution (see JP-A-57-12487) to the active material mixture.

The surface of the positive electrode active material may be modified by treating with an esterification agent (see JP-A-55-163779), a chelating agent (see JP-A-55-163780), a conducting high polymer (see JP-A-58-163188 and JP-A-59-14274), polyethylene oxide (see JP-A-60-97561), and the like.

The surface of the negative electrode active material may also be modified by, for example, providing a layer comprising an ion-conductive polymer or polyacetylene (see JP-A-58-111276) or treating with LiCl (see JP-A-58-142771).

A collector for an active material may be made of any electron-conducting substance which undergoes no chemical change in an assembled battery. Suitable materials of a collector for the positive electrode include stainless steel, nickel, aluminum, titanium, calcined carbon; and aluminum or stainless steel with its surface treated with carbon, nickel, titanium or silver. Suitable materials of a collector for the negative electrode include stainless steel, nickel, copper, titanium, aluminum, calcined carbon; copper or stainless steel with its surface treated with carbon, nickel, titanium or silver; and an Al-Cd alloy. These materials may be subjected to surface oxidation. The collector may have a variety of forms, such as a foil, a film, a sheet, a net, a punched sheet, a lath, a porous body, a foamed body, a fibrous body, and so on. While not limiting, the thickness of the collector is from 1 to 500 μm .

The battery according to the present invention may have any shape, such as a coin shape, a button shape, a sheet shape, a cylindrical shape, and an angular shape.

A coin-shaped or button-shaped battery is generally produced by compressing a positive or negative active material mixture into a pellet having prescribed thickness and diameter according to the size of the battery. A sheet, cylindrical or angular battery is generally produced by coating a collector with a positive or negative active material mixture, followed by drying and compressing. The thickness, length or width of the coating layer are decided according to the size of the battery. In particular, the dry thickness (thickness after compression) is preferably selected from the range 1 to 2000 μm .

The application of the nonaqueous secondary battery of the present invention is not particularly limited. For example, it is useful in electronic equipment, such as notebook-size color or monochromatic personal computers, pen input personal computers, pocket-size (palmtop) personal computers, notebook-size word processors, pocket-size word processors, electron book players, pocket phones, wireless extensions of key telephone sets, pagers, handy terminals, portable facsimiles, portable copying machines, portable printers, headphone stereos, video cameras, liquid crystal TV sets, handy cleaners, portable CD, mini disk systems, electrical shavers, machine translation systems, land mobile radiotelephones, transceivers, electrical tools, portable calculators, memory cards, tape recorders, radios, backup powers, and so on; automobiles, electrically-powered vehicles, motors, lights, toys, family (home) computers, load conditioners, irons, watches, stroboscopic lamps, cameras, medical equipment (e.g., pacemakers, hearing aids, and massaging machines); military equipment; and spacecraft equipment. The nonaqueous secondary battery of the present invention may be used in combination with solar batteries.

The present invention will now be illustrated in greater detail with reference to Examples, but the present invention should not be construed as being limited thereto. All the percents are by weight unless otherwise indicated.

SYNTHESIS EXAMPLE B-1

Tin monoxide (13.5 g) and silicon dioxide (6.0 g) were dry blended, put in an alumina crucible, heated up to 1000°C at a rate of 10°C/min in an argon atmosphere, calcined at that temperature for 12 hours, cooled to room temperature at a rate of 6°C/min, and taken out of the calcination furnace to obtain SnSiO_3 . The calcined product was coarsely ground and further pulverized in a jet mill to an average particle size of 5 μm (hereinafter designated as compound B-1-A).

In the same manner, the following compounds were synthesized starting with the stoichiometric amounts of the respective raw materials.

SnGeO_3 (compound B-1-B)
 SnPbO_3 (compound B-1-C)
 $\text{SnSi}_{0.9}\text{Ge}_{0.1}\text{O}_3$ (compound B-1-D)
 $\text{SnSi}_{0.9}\text{Pb}_{0.1}\text{O}_3$ (compound B-1-E)
 $\text{SnSi}_{0.5}\text{Ge}_{0.5}\text{O}_3$ (compound B-1-F)
 $\text{SnSi}_{0.5}\text{Pb}_{0.5}\text{O}_3$ (compound B-1-G)
 $\text{SnGe}_{0.9}\text{Pb}_{0.1}\text{O}_3$ (compound B-1-H)
 $\text{SnSi}_{0.7}\text{O}_{2.4}$ (compound B-1-I)
 $\text{SnSi}_{1.2}\text{O}_{3.4}$ (compound B-1-J)
 $\text{SnSi}_{1.5}\text{O}_4$ (compound B-1-K)
 PbSiO_3 (compound B-1-L)
 PbGeO_3 (compound B-1-M)
 $\text{PbSi}_{0.9}\text{Ge}_{0.1}\text{O}_3$ (compound B-1-N)

SYNTHESIS EXAMPLE B-2

Tin monoxide (13.5 g) and silicon dioxide (6.0 g) were dry blended, put in an alumina crucible, heated up to 1000°C at a rate of 10°C/min in an argon atmosphere, calcined at that temperature for 12 hours, and spread on a stainless steel foil in an argon atmosphere for quenching. The resulting product was coarsely ground and further pulverized in a jet mill to obtain SnSiO_3 having an average particle size of 5 μm (hereinafter designated as compound B-2-A).

SYNTHESIS EXAMPLE B-3

Tin dioxide (15.1 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, calcined at 1000°C for 12 hours in air, cooled to room temperature, and taken out of the calcination furnace to obtain $\text{SnSi}_{0.1}\text{O}_{2.2}$. The calcined product was pulverized in a jet mill to an average particle size of 4 μm (hereinafter designated as compound B-3-A).

In the same manner, the following compounds were synthesized starting with the stoichiometric amounts of the respective raw materials.

$\text{SnSi}_{0.3}\text{O}_{2.6}$ (compound B-3-B)
 $\text{SnGe}_{0.1}\text{O}_{2.2}$ (compound B-3-C)
 $\text{SnGe}_{0.3}\text{O}_{2.6}$ (compound B-3-D)
 $\text{SnPb}_{0.1}\text{O}_{2.2}$ (compound B-3-E)
 $\text{SnPb}_{0.1}\text{O}_{2.6}$ (compound B-3-F)
 $\text{SnSi}_{0.1}\text{Ge}_{0.1}\text{O}_{2.4}$ (compound B-3-G)
 $\text{SnSi}_{0.1}\text{Pb}_{0.1}\text{O}_{2.4}$ (compound B-3-H)
 $\text{SnSi}_{0.01}\text{O}_{2.02}$ (compound B-3-I)
 $\text{SnSi}_{1.5}\text{O}_5$ (compound B-3-J)
 SnSi_2O_6 (compound B-3-K)
 $\text{PbSi}_{0.1}\text{O}_{2.2}$ (compound B-3-L)
 $\text{PbGe}_{0.3}\text{O}_{2.6}$ (compound B-3-M)
 $\text{GeSi}_{0.1}\text{O}_{2.2}$ (compound B-3-N)
 $\text{GeSi}_{0.3}\text{O}_{2.6}$ (compound B-3-O)

SYNTHESIS EXAMPLE B-4

Tin monoxide (13.5 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, calcined at 350°C for 6 hours in an argon atmosphere, cooled to room temperature, and taken out of the calcination furnace to obtain $\text{SnSi}_{0.1}\text{O}_{1.2}$. The calcined product was pulverized in a jet mill to an average particle size of 2 μm (compound B-4-A).

In the same manner, the following compounds were synthesized starting with the stoichiometric amounts of the respective raw materials.

SnSi_{0.01}O_{1.02} (compound B-4-B)
 SnGe_{0.1}O_{1.2} (compound B-4-C)
 SnPb_{0.1}O_{1.2} (compound B-4-D)
 PbSi_{0.05}O_{1.1} (compound B-4-E)
 PbGe_{0.1}O_{1.1} (compound B-4-F)
 GeSiO₃ (compound B-4-G).

EXAMPLE B-1

A coin lithium battery having the structure shown in Fig. 2 was assembled in a dry box (dry air; dew point: -40° to -70°C) using the following materials.

Electrode

A negative electrode active material mixture consisting of 82% of each of compounds B-1-A to N synthesized in Synthesis Example B-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded to obtain a negative electrode pellet of 13 mm in diameter and 22 mg in weight. Before use, the pellet was dried in the above-described dry box by means of a far infrared heater at 150°C for 3 hours.

Counter Electrode:

A positive electrode active material mixture consisting of 82% of LiCoO₂ as a positive electrode active material, 8% of flake graphite, 4% of acetylene black, and 6% of tetrafluoroethylene was compression molded to obtain a pellet of 13 mm in diameter. The weight of the pellet was decided according to the lithium intercalation capacity of the negative electrode active material precursor, and the charge capacity of LiCoO₂ was 170 mAh/g. Before use, the pellet was dried in the same dry box as used above at 150°C for 3 hours by means of a far infrared heater.

Collector:

A 80 μm thick net of SUS316 was welded to each of the positive electrode case and the negative electrode case.

Electrolytic Solution:

200 μl of a 1 mol/l solution of LiPF₆ in a 2:2:6 (by volume) mixture of ethylene carbonate, butylene carbonate and dimethyl carbonate.

Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electrolytic solution.

The resulting lithium battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm², a cut-off voltage of 4.3 V in charging, and a cut-off voltage of 2.7 V in discharging. All the tests were started with charging. The results obtained are shown in Table B-1.

Symbols used in Table B-1 and Tables B-2 to B-7 hereinafter described have the following meanings:

- (a) negative electrode active material of the present invention
- (b) discharge capacity of the first cycle (mAh/g-negative electrode active material)
- (c) average discharge potential (V)
- (d) cycle characteristics (the number of the cycles at which the discharge capacity was reduced to 60% of that of the first cycle)

TABLE B-1

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
2	B-1-B	448	3.54	289
3	B-1-C	495	3.35	305
8	B-1-H	440	3.50	267
13	B-1-M	389	3.25	248

The results in Table B-1 reveal that the negative electrode active material according to the present invention provides a nonaqueous secondary battery having excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

EXAMPLE B-3

Coin batteries were prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with each of compounds B-3-A to B-3-O synthesized in Synthesis Example B-3. The results obtained are shown in Table B-3.

TABLE B-3

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
3	B-3-C	458	3.53	166
4	B-3-D	472	3.51	158
5	B-3-E	481	3.47	161
6	B-3-F	482	3.42	159
13	B-3-M	401	3.38	155

It can be seen that the battery using the negative electrode active material according to the present invention have excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

EXAMPLE B-4

Coin batteries were prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with each of compounds B-4-A to B-4-G synthesized in Synthesis Example B-4. The results obtained are shown in Table B-4.

TABLE B-4

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
3	B-4-C	472	3.55	141
4	B-4-D	492	3.49	155
6	B-4-F	428	3.28	116

It can be seen that the battery using the negative electrode active material according to the present invention has excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

COMPARATIVE EXAMPLE B-1

A coin battery was prepared and tested in the same manner as in Example B-1, except for replacing the compound

B-1 as a negative electrode active material with SnO_2 or SnO . The results obtained are shown in Table B-5.

TABLE B-5

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	SnO_2	443	3.48	85
2	SnO	483	3.53	73

It is seen that the use of the tin compound oxide according to the present invention as a negative electrode active material provides a battery superior to that using SnO_2 or SnO in terms of charge and discharge cycle characteristics and capacity.

COMPARATIVE EXAMPLE B-2

A coin battery was prepared and tested in the same manner as in Example B-1, except for replacing the compound B-1 as a negative electrode active material with WO_2 or Fe_2O_3 . The results obtained are shown in Table B-6.

TABLE B-6

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	WO_2	163	3.21	42
2	Fe_2O_3	109	3.16	13

It is apparent that the use of the tin compound oxide according to the present invention as a negative electrode active material provides a battery superior to that using WO_2 or Fe_2O_3 in terms of all of charge and discharge cycle characteristics, discharge potential, and capacity.

SYNTHESIS EXAMPLE D-1

Tin monoxide (13.5 g) and silicon dioxide (6.0 g) were dry blended, put in an alumina crucible, heated up to 1000°C at a rate of $15^\circ\text{C}/\text{min}$ in an argon atmosphere, calcined at that temperature for 12 hours, cooled to room temperature at a rate of $10^\circ\text{C}/\text{min}$, and taken out of the calcination furnace to obtain SnSiO_3 . The calcined product was pulverized in a jet mill to an average particle size of $4.5\ \mu\text{m}$ (hereinafter designated as compound D-1-A).

The X-ray diffraction pattern ($\text{CuK}\alpha$ rays) of compound D-1-A is shown in Fig. 1. The pattern shows a broad peak centered at about 28° (2θ) with no diffraction assigned to crystal properties between 40° and 70° (2θ).

The following compounds were also synthesized in the same manner as described above using stoichiometrical amounts of the respective starting materials. The X-ray diffraction pattern ($\text{CuK}\alpha$ rays) of these compounds similarly exhibited a broad scattering band with its peak between 20° and 40° (2θ). The diffraction intensity of the peak of the broad scattering band appearing between 20° and 40° (2θ) is taken as A, and the strongest intensity of any diffraction line assigned to crystal properties which may appear between 40° and 70° (2θ) is taken as B (B = 0 where no diffraction assigned to crystal properties occurs). The B/A value is shown together with the compound number.

SnGeO_3 (compound D-1-B; B/A = 0)

$\text{SnSi}_{0.8}\text{P}_{0.1}\text{O}_3$ (compound D-1-C; B/A = 0)

$\text{SnSi}_{0.9}\text{Ge}_{0.1}\text{O}_3$ (compound D-1-D; B/A = 0)

$\text{SnSi}_{0.9}\text{Pb}_{0.1}\text{O}_3$ (compound D-1-E; B/A = 0)

$\text{SnSi}_{0.5}\text{Ge}_{0.6}\text{O}_3$ (compound D-1-F; B/A = 0)

$\text{SnSi}_{0.5}\text{Pb}_{0.5}\text{O}_3$ (compound D-1-G; B/A = 0.3)

$\text{SnGe}_{0.9}\text{Pb}_{0.1}\text{O}_3$ (compound D-1-H; B/A = 0)

$\text{SnSi}_{0.8}\text{O}_{2.4}$ (compound D-1-I; B/A = 0.1)

$\text{SnSi}_{1.2}\text{O}_{3.4}$ (compound D-1-J; B/A = 0)

$\text{SnSi}_{1.5}\text{O}_4$ (compound D-1-K; B/A = 0)

PbSiO_3 (compound D-1-L; B/A = 0)

PbGeO_3 (compound D-1-M; B/A = 0)

PbSi_{0.9}Ge_{0.1}O₃ (compound D-1-N; B/A = 0)

SnPO_{3.5} (compound D-1-O; B/A = 0)

SnBO_{2.5} (compound D-1-P; B/A = 0)

SnSi_{0.9}O_{2.8} (compound D-1-Q; B/A = 0)

SYNTHESIS EXAMPLE D-2

Tin monoxide (1.35 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, heated up to 1000°C at a rate of 15°C/min in an argon atmosphere, calcined at that temperature for 10 hours, and quenched by spreading on a stainless steel foil in an argon atmosphere. The calcined product (SnSiO₃) was coarsely ground and then pulverized in a jet mill to an average particle size of 3.5 μm (hereinafter designated as compound D-2-A). The B/A ratio in the X-ray diffraction pattern was 9.5.

SYNTHESIS EXAMPLE D-3

Tin dioxide (15.1 g) and silicon dioxide (0.6 g) were dry blended, put in an alumina crucible, calcined at 1200°C for 10 hours, cooled to room temperature, and taken out of the furnace to obtain SnSi_{0.1}O_{2.2}. The calcined product was pulverized in a jet mill to an average particle size of 4 μm (hereinafter designated as compound D-3-A). The B/A ratio in the X-ray diffraction pattern was 0.

In the same manner as above, the following compounds were synthesized using stoichiometrical amounts of the respective starting materials.

SnSi_{0.3}O_{2.8} (compound D-3-B; B/A = 2.4)

SnGe_{0.1}O_{2.2} (compound D-3-C; B/A = 7.4)

SnGe_{0.3}O_{2.6} (compound D-3-D; B/A = 4.7)

SnPb_{0.1}O_{2.2} (compound D-3-E; B/A = 7.5)

SnPb_{0.1}O_{2.8} (compound D-3-F; B/A = 16.5)

SnSi_{0.1}Ge_{0.1}O_{2.4} (compound D-3-G; B/A = 9.5)

SnSi_{0.1}Pb_{0.1}O_{2.4} (compound D-3-H; B/A = 29.1)

SnSi_{0.01}O_{2.02} (compound D-3-I; B/A = 7.1)

SnSi_{1.3}O₅ (compound D-3-J; B/A = 0)

SnSi₂O₆ (compound D-3-K; B/A = 0)

PbSi_{0.1}O_{2.2} (compound D-3-L; B/A = 5.3)

PbGe_{0.3}O_{2.6} (compound D-3-M; B/A = 2.3)

GeSi_{0.1}O_{2.2} (compound D-3-N; B/A = 0)

GeSi_{0.2}O_{2.6} (compound D-3-O; B/A = 0)

SnP_{0.3}O_{2.75} (compound D-3-P; B/A = 1.4)

SnB_{0.3}O_{2.45} (compound D-3-Q; B/A = 6.4)

SYNTHESIS EXAMPLE D-4

Tin monoxide (13.5 g), 4.8 g of silicon dioxide, and 1.42 g of diphosphorus pentoxide, each weighed in dry air having a dew point of -50°C, were dry blended in a ball mill in the same dry air. The mixture was put in an alumina crucible, heated to 1100°C at a rate of 10°C/min in an argon atmosphere, calcined at that temperature for 10 hours, and cooled to room temperature at a rate of 8.3°C/min to obtain a glassy compound. The compound was pulverized in a jet mill and air-classified to obtain compound D-4-A having an average particle size of 4 μm. The B/A ratio in the X-ray diffraction pattern was 0.

In the same manner as described above, the following compounds were synthesized using stoichiometrical amounts of the respective starting materials (Al₂O₃ and Sb₂O₃ were used as an Al source and an Sb source, respectively).

SnSi_{0.9}P_{0.1}O_{3.05} (compound D-4-B; B/A = 0)

SnSi_{0.7}P_{0.9}O_{3.15} (compound D-4-C; B/A = 0)

SnSi_{0.5}P_{0.5}O_{3.25} (compound D-4-D; B/A = 0)

SnSi_{0.2}P_{0.8}O_{3.4} (compound D-4-E; B/A = 0)

SnSi_{0.8}P_{0.1}Sb_{0.1}O₃ (compound D-4-F; B/A = 0.5)

SYNTHESIS EXAMPLE D-5

Tin monoxide (10.78 g), 3.6 g of silicon dioxide, 4.11 g of stannous pyrophosphate, and 2.1 g of germanium dioxide were dry blended in a ball mill. The mixture was put in an alumina crucible, heated to 1100°C at a rate of 10°C/min in an argon atmosphere, and calcined at that temperature for 10 hours. The calcined product was quenched by pouring into water in an argon atmosphere to obtain a glassy compound. The compound was wet ground in a ball mill using water as a grinding medium, and the slurry was passed through a sieve of 25 µm to remove coarse particles. Water was removed by decantation, and the solid was dried at 150°C for 1 hour to obtain compound D-5-A having an average particle size of 3.1 µm. The B/A ratio in the X-ray diffraction pattern was 0.

In the same manner as described above, the following compounds were synthesized using stoichiometrical amounts of the respective starting materials. Al₂O₃ was used as an aluminum source.

SnSi_{0.7}Ge_{0.1}P_{0.2}O_{3.1} (compound D-5-B; B/A = 0)

SnSi_{0.6}Ge_{0.4}P_{0.1}O_{3.25} (compound D-5-C; B/A = 0)

SnSi_{0.2}Ge_{0.1}P_{0.7}O_{3.35} (compound D-5-D; B/A = 0)

SnSi_{0.8}P_{0.1}Al_{0.1}O₃ (compound D-5-E; B/A = 0)

SnSi_{0.8}P_{0.2}Al_{0.1}O_{3.25} (compound D-5-F; B/A = 0)

SnSi_{0.6}P_{0.1}Al_{0.3}O_{2.9} (compound D-5-G; B/A = 0)

SnSi_{0.6}P_{0.3}Al_{0.1}O_{3.1} (compound D-5-H; B/A = 0)

SnSi_{0.3}P_{0.7}Al_{0.1}O_{3.5} (compound D-5-I; B/A = 1.5)

SnSi_{0.8}P_{0.2}O_{3.1} (compound D-5-J; B/A = 0)

SnSi_{0.6}P_{0.4}Al_{0.2}O_{3.5} (compound D-5-K; B/A = 0)

SnSi_{0.1}P_{0.9}Al_{0.1}O_{3.6} (compound D-5-L; B/A = 0)

SnSi_{0.8}Al_{0.2}P_{0.2}O_{3.4} (compound D-5-M; B/A = 0)

SnSi_{0.7}Al_{0.2}P_{0.3}P_{3.45} (compound D-5-N; B/A = 0)

SnSi_{0.4}Al_{0.2}P_{0.6}O_{3.6} (compound D-5-O; B/A = 0)

SnPAl_{0.1}O_{3.65} (compound D-5-P; B/A = 0)

EXAMPLE D-1

A coin-shaped nonaqueous battery having the structure shown in Fig. 2 was assembled in a dry box (dew point: -40° to -70°C; dry air) using the following materials.

Electrode:

A negative electrode active material mixture consisting of 82% of each of compounds D-1-A to D-1-Q synthesized in Synthesis Example D-1, 8% of flake graphite and 4% of acetylene black as conducting agents, and 6% of polyvinylidene fluoride as a binder was compression molded into a pellet of 13 mm in diameter and 22 mg in weight. Before use, the pellet was dried in the above-described dry box by means of a far infrared heater at 150°C for 3 hours.

Counter Electrode:

A positive electrode active material mixture consisting of 82% of LiCoO₂ as a positive electrode active material, 8% of flake graphite, 4% of acetylene black, and 6% of tetrafluoroethylene was compression molded to obtain a pellet of 13 mm in diameter (the weight was decided according to the lithium intercalation capacity of the compound D-1). The charge capacity of LiCoO₂ was 170 mAh/g. Before use, the pellet was dried in the same dry box as used above at 150°C for 3 hours by means of a far infrared heater.

Collector:

A 80 µm thick net of SUS316 was welded to each of the positive case and the negative case.

Electrolytic Solution:

200 µl of a 1 mol/l solution of LiPF₆ in a 2:2:6 (by volume) mixed solvent of ethylene carbonate, butylene carbonate and dimethyl carbonate.

Separator:

A finely porous polypropylene sheet and polypropylene nonwoven fabric impregnated with the electrolytic solution.

The resulting nonaqueous battery was subjected to a charge and discharge test under conditions of a constant current density of 0.75 mA/cm² and a voltage between 4.3 V and 2.7 V. All the tests were started with charging. The results obtained are shown in Table D-1.

Symbols used in Table D-1 and Tables D-2 to D-10 hereinafter shown have the following meanings:

- (a) negative electrode active material of the present invention
- (b) discharge capacity of the first cycle (mAh/g-negative electrode active material)
- (c) average discharge potential (V)
- (d) cycle characteristics (the number of cycles at which the discharge capacity was reduced to 60% of the initial discharge capacity).

TABLE D-1

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
2	D-1-B	452	3.52	296
8	D-1-H	428	3.53	268
13	D-1-M	395	3.21	262
15	D-1-O	462	3.54	302
16	D-1-P	472	3.55	288

It is seen from these results that the negative electrode active material according to the present invention provides a nonaqueous secondary battery having excellent charge and discharge cycle characteristics with a high discharge potential and a high capacity.

EXAMPLE D-3

Coin batteries were prepared and tested in the same manner as in Example D-1, except for replacing the compound D-1 with each of compounds D-3-A to D-3-Q synthesized in Synthesis Example D-3 as a negative electrode active material. The results obtained are shown in Table D-3.

TABLE D-3

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
3	D-3-C	459	3.51	177
4	D-3-D	478	3.53	163
5	D-3-E	487	3.45	169
6	D-3-F	489	3.48	164
13	D-3-M	409	3.42	202
16	D-3-P	457	3.40	212
17	D-3-Q	463	3.41	211

It can be seen that the batteries using the negative electrode active material according to the present invention have excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity.

COMPARATIVE EXAMPLE D-1

A coin battery was prepared and tested in the same manner as in Example D-1, except for using, as a negative electrode active material, SnO_2 or SnO . The SnO_2 and SnO used here showed no broad scattering band assigned to amorphous properties in its X-ray diffractometry using $\text{CuK}\alpha$ rays. The results obtained are shown in Table D-4.

TABLE D-4

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	SnO_2	443	3.48	85
2	SnO	483	3.53	73

It is apparent that the use of the tin compound oxide according to the present invention as a negative electrode active material provides a battery superior to that using SnO_2 or SnO in terms of charge and discharge cycle characteristics and capacity.

COMPARATIVE EXAMPLE D-2

A coin battery was prepared and tested in the same manner as in Example D-1, except for using, as a negative electrode active material, Fe_2O_3 , amorphous V_2O_5 , or LiCoVO_4 . The results obtained are shown in Table D-5.

TABLE D-5

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	Fe_2O_3	109	3.16	13
2	V_2O_5	82	2.83	82
3	LiCoVO_4	256	2.91	102

It is seen that the battery using the tin compound oxide according to the present invention as a negative electrode active material is superior to that using Fe_2O_3 , amorphous V_2O_5 , or LiCoVO_4 in terms of charge and discharge cycle characteristics, discharge potential, and discharge capacity.

EXAMPLE D-4

A coin nonaqueous secondary battery was prepared and tested in the same manner as in Run No. 1 of Example D-1, except for replacing LiCoO_2 with each of the positive electrode active materials shown in Table D-6. The results obtained are shown in Table D-6.

TABLE D-6

Run No.	Positive Electrode Active Material	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	LiCoO_2	493	3.5	335
2	LiNiO_2	497	3.39	340
3	$\text{LiCo}_{0.95}\text{V}_{0.05}\text{O}_{2.0}$	485	3.49	390
4	LiMn_2O_4	474	3.54	329
5	LiMnO_2	505	3.31	330

It is seen that the negative electrode active material of the present invention provides a nonaqueous secondary battery excellent in all of charge and discharge cycle characteristics, discharge potential, and discharge capacity regardless of which of these positive electrode active materials is used.

COMPARATIVE EXAMPLE D-4

SnSiO₃ (compound D-1-A) synthesized in Synthesis Example D-1 was heat treated at 700°C for 2 hours and cooled to room temperature to obtain crystalline SnSiO₃. The X-ray diffraction pattern of the product showed no peak assigned to amorphous properties. A coin battery was prepared and tested in the same manner as in Example D-1, except for using the thus prepared crystalline SnSiO₃ as a negative electrode active material. The results of the charge and discharge test are shown in Table D-8.

TABLE D-8

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
1	SnSiO ₃ (crystalline)	441	3.48	95

It can be seen that the nonaqueous secondary battery prepared by using the amorphous tin compound oxide of the present invention as a negative electrode active material is superior in charge and discharge cycle characteristics and capacity to that prepared by using a crystalline tin compound oxide.

EXAMPLE D-7

A coin battery was prepared and tested in the same manner as in Run No. 1 of Example D-1, except for replacing compound D-1-A as a negative electrode active material with each of compounds D-4-A to F synthesized in Synthesis Example D-4 and compounds D-5-A to P synthesized in Synthesis Example D-5. The results of the charge and discharge test are shown in Table D-9.

TABLE D-9

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)
22	D-5-P	562	3.52	372

The results prove that the negative electrode active materials which can be used in the present invention provide a nonaqueous secondary battery with excellent charge and discharge cycle characteristics, a high discharge potential, and a high capacity. It is also seen that batteries using a P-containing compound as a negative electrode active material are particularly excellent in charge and discharge cycle characteristics.

EXAMPLE D-8

A coin battery was prepared and tested in the same manner as in Example D-4, except for replacing compound D-1-A as a negative electrode active material with each of compounds D-4-A to F synthesized in Synthesis Example D-4 and compounds D-5-A to P synthesized in Synthesis Example D-5. The results of the charge and discharge test are shown in Table D-10. In Table D-10, symbol (e) has the same meaning as in Table D-7.

TABLE D-10

Run No.	(a)	(b) (mAh/g)	(c) (V)	(d) (cycles)	(e) (mAh/ml)
22	D-5-P	561	3.56	584	413

As described above, the use of an Li-containing transition metal oxide as a positive electrode active material and at least one specific compound oxide as a negative electrode active material affords a nonaqueous secondary battery having a high discharge potential, a high discharge capacity and excellent charge and discharge cycle characteristics.

Claims

1. A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt, wherein said negative electrode active material contains at least one compound capable of intercalating and deintercalating lithium mainly comprising a compound represented by formula (I):



wherein M^1 and M^2 , which are different from each other, each represent at least one of Ge, Sn, Pb, P, B, Al, As, and Sb; M^4 represents at least one of O, S, Se, and Te; p represents a number of from 0.001 to 10; and q represents a number of from 1.00 to 50.

2. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material mainly comprises an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB, and VB of the periodic table.

3. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material contains at least one compound of the atom of the group IIIB, IVB, or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium.

4. A nonaqueous secondary battery as claimed in claim 1, wherein the atom of the group IIIB, IVB and VB of the periodic table is selected from the group consisting of Al, Ge, Sn, Pb, As, and Sb.

5. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material is a compound which is amorphous at the time of intercalating lithium ion.

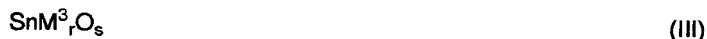
6. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material is a compound which is amorphous at the time of assembling a battery.

7. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material mainly comprises a compound represented by formula (II):



wherein M^3 represents at least one of Ge, Pb, P, B, Al, As, and Sb; M^5 represents at least one of O and S; p represents a number of from 0.001 to 10; and q represents a number of from 1.00 to 50.

8. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material mainly comprises a compound oxide represented by formula (III):



wherein M^3 represents at least one of Ge, Pb, P, B, Al, and As; r represents a number of from 0.01 to 5.0; and s represents a number of from 1.0 to 26.

9. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material is obtained by a calcination method consisting of heating at a rate of temperature rise of 4° to $2,000^\circ\text{C}/\text{min}$, maintaining at 250° to $1,500^\circ\text{C}$ for 0.01 to 100 hours, and cooling at a rate of temperature drop of 2° to $10^7^\circ\text{C}/\text{min}$.

10. A nonaqueous secondary battery as claimed in claim 1, wherein said negative electrode active material is obtained by a calcination method consisting of heating at a rate of temperature rise of 10° to $2,000^\circ\text{C}/\text{min}$, maintaining at 250° to $1,500^\circ\text{C}$ for 0.01 to 100 hours, and cooling at a rate of temperature drop of 2° to $10^7^\circ\text{C}/\text{min}$.

11. A nonaqueous secondary battery as claimed in claim 1, wherein said positive electrode active material is a lithium-containing transition metal oxide.

12. A nonaqueous secondary battery as claimed in claim 1, wherein said positive electrode active material contains at least one compound represented by formula $Li_x QO_y$, wherein Q represents at least one transition metal selected from Co, Mn, Ni, V, and Fe; x is from 0.2 to 1.2; and y is from 1.4 to 3.

13. A nonaqueous secondary battery as claimed in claim 1, wherein said positive electrode active material contains at least one compound selected from $Li_x CoO_2$, $Li_x NiO_2$, $Li_x MnO_2$, $Li_x Co_a Ni_{1-a} O_2$, $Li_x Co_b V_{1-b} O_2$, $Li_x Co_c Fe_{1-c} O_2$, $Li_x Mn_2 O_4$, $Li_x Mn_c Co_{2-c} O_4$, $Li_x Mn_c Ni_{2-c} O_4$, $Li_x Mn_c V_{2-c} O_4$, and $Li_x Mn_c Fe_{2-c} O_4$ (wherein $x = 0.7$ to 1.2 ; $a = 0.1$ to 0.9 ; $b = 0.8$ to 0.98 ; $c = 1.6$ to 1.96 ; $z = 2.01$ to 2.3).

EP 0 814 522 A2

14. A nonaqueous secondary battery as claimed in claim 1, wherein said positive electrode active material is a lithium-containing manganese compound having a spinel structure and a stoichiometric or non-stoichiometric composition.

5 15. A nonaqueous secondary battery as claimed in claim 1, wherein lithium is intercalated in an amount of from 1 to 20 equivalents.

10

15

20

25

30

35

40

45

50

55

FIG. 1

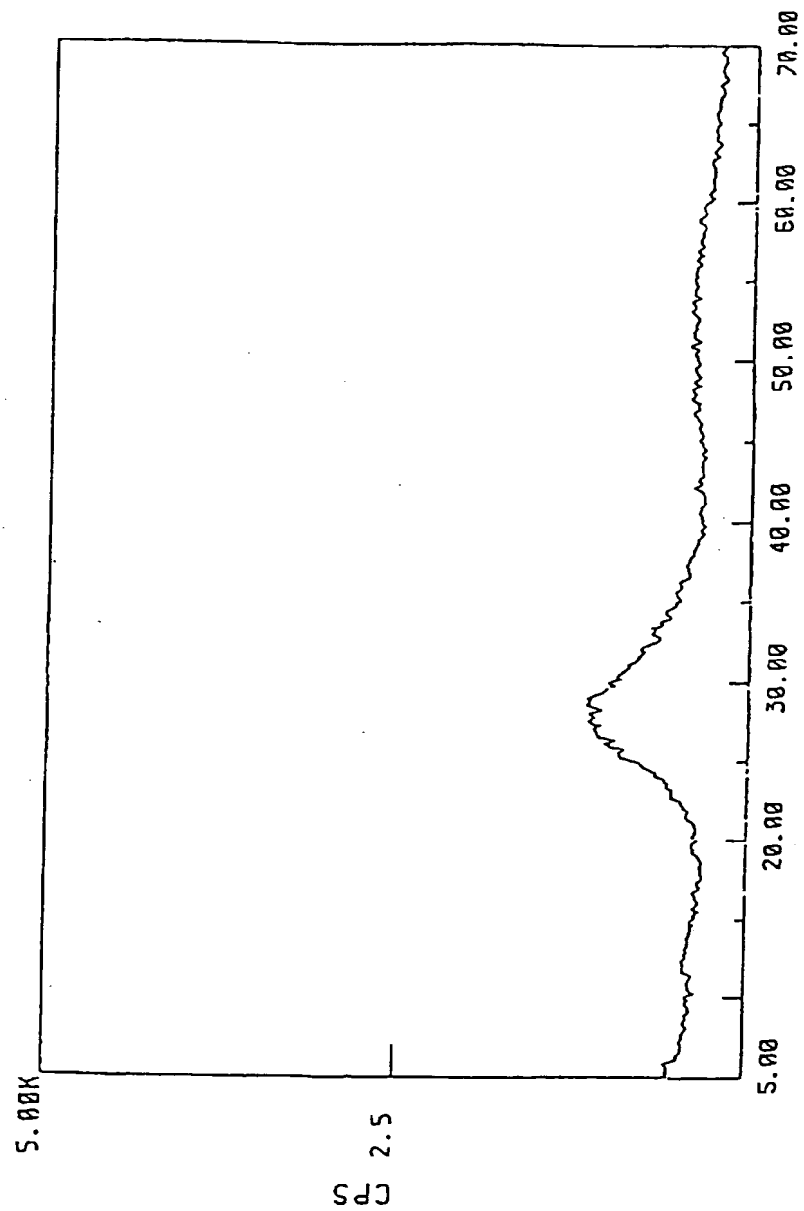


FIG. 2

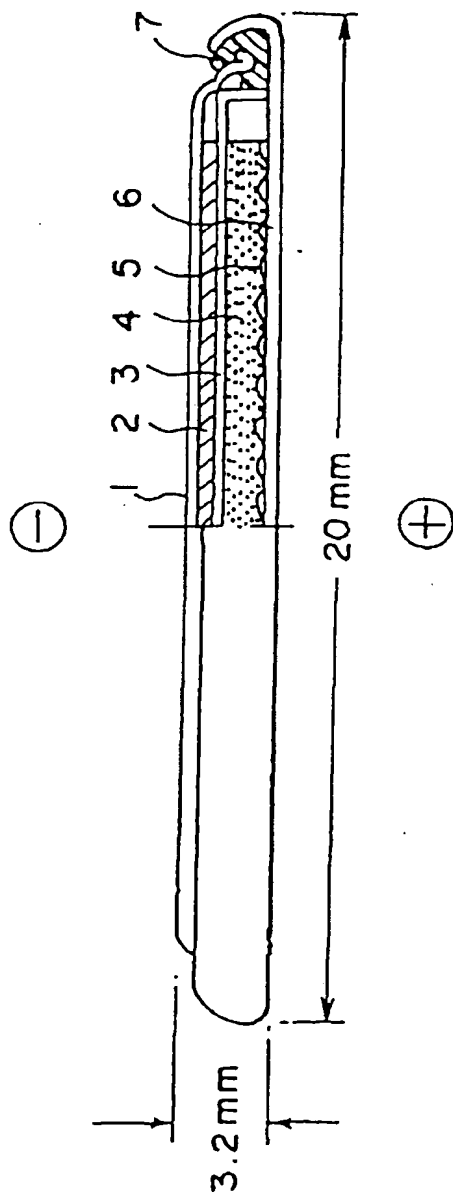
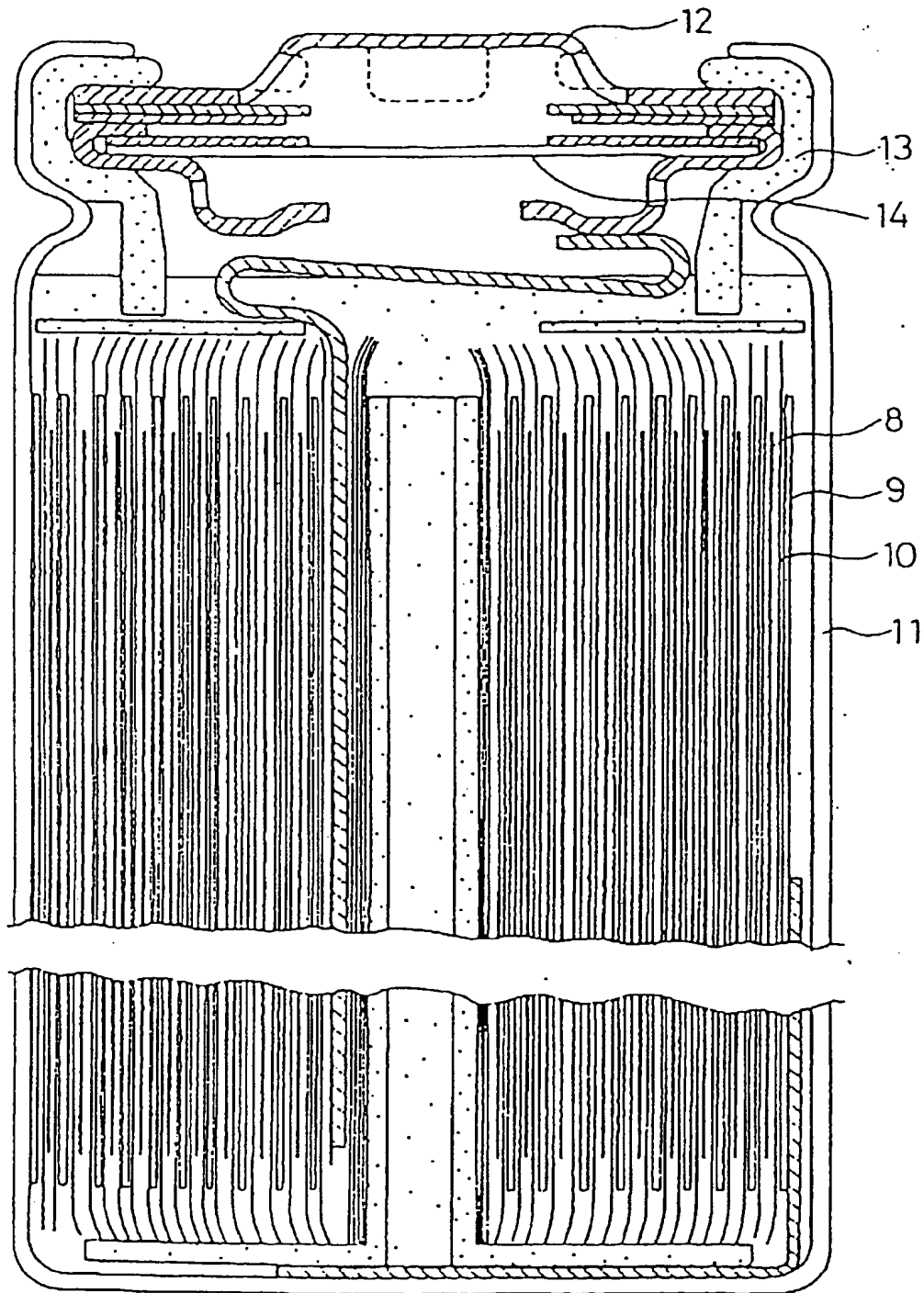


FIG. 3



(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 814 522 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
12.05.1999 Bulletin 1999/19

(51) Int. Cl.⁶: **H01M 4/48**, H01M 4/58,
H01M 10/40

(43) Date of publication A2:
29.12.1997 Bulletin 1997/52

(21) Application number: 97110038.3

(22) Date of filing: 21.10.1994

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 22.10.1993 JP 264995/93
27.01.1994 JP 7760/94
24.02.1994 JP 26745/94
28.02.1994 JP 30206/94
11.03.1994 JP 66422/94

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
94116643.1 / 0 651 450

(71) Applicant:
FUJI PHOTO FILM CO., LTD.
Kanagawa-ken (JP)

(72) Inventors:

- Idota, Yoshio
Minami-Ashigara-shi, Kanagawa-ken (JP)
- Mishima, Masayuki
Minami-Ashigara-shi, Kanagawa-ken (JP)
- Miyaki, Yukio
Minami-Ashigara-shi, Kanagawa-ken (JP)
- Kubota, Tadahiko
Minami-Ashigara-shi, Kanagawa-ken (JP)
- Miyasaka, Tsutomu
Minami-Ashigara-shi, Kanagawa-ken (JP)

(74) Representative:

Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann Eitle,
Patent- und Rechtsanwälte,
Arabellastrasse 4
81925 München (DE)

(54) Nonaqueous secondary battery

(57) A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt is disclosed, in which the negative electrode active material contains (1) a compound capable of intercalating and deintercalating lithium, comprising an atom of the group IIIB, IVB (except for Si) or VB of the periodic table, (2) an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB (except for Si), and VB of the periodic table, or (4) a compound of the metal of the group IIIB, IVB (except for Si) or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium. The nonaqueous secondary battery of the invention exhibits improved charge and discharge characteristics and improved safety.

EP 0 814 522 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 0038

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 5 147 739 A (BEARD KIRBY W) 15 September 1992 * claim 1 *	1, 11-15	H01M4/48 H01M4/58 H01M10/40
A	EP 0 205 856 A (ASAHI CHEMICAL IND) 30 December 1986 * claim 1 *	1, 7, 11-15	
P, A	"CHEMICAL ABSTRACTS + INDEXES" CHEMICAL ABSTRACTS + INDEXES, XP000664954 * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 March 1999	Examiner Andrews, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 11 0038

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-03-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5147739	A	15-09-1992	NONE	
<hr/>				
EP 0205856	A	30-12-1986	CA 1265580 A	06-02-1990
			HK 93393 A	17-09-1993
			JP 1989293 C	08-11-1995
			JP 4024831 B	28-04-1992
			JP 62090863 A	25-04-1987
			JP 2704841 B	26-01-1998
			JP 7176302 A	14-07-1995
			JP 2727301 B	11-03-1998
			JP 7176303 A	14-07-1995
			US RE34991 E	04-07-1995
			US 4668595 A	26-05-1987
<hr/>				

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)